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[54] **COLOR DECALCOMANIA AND METHOD**

[75] Inventors: **Louis A. Blanco**, Tuckahoe, N.Y.; **William F. Wenning, Jr.**, Beaver Falls, Pa.

[73] Assignee: **Commercial Decal, Inc.**, Mount Vernon, N.Y.

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[51] **Int. Cl.** **C04b 37/00,** B41m 3/12

[58] **Field of Search** 117/3.1–3.6, 117/45; 156/89, 230, 236, 240, 249

[56] **References Cited**

UNITED STATES PATENTS

2,216,017	9/1940	Matthes	117/38
2,324,433	7/1943	Sheetz	117/40 X
2,629,679	2/1953	Rathke	117/3.4 X
2,734,840	2/1956	Kane	161/413 X
3,007,829	11/1961	Akkeron	117/3.2 X
3,089,782	5/1963	Bush et al.	117/40 X
3,290,232	12/1966	Dunning	117/3.6 X
3,656,984	4/1972	Hoffman	106/49 X

Primary Examiner—Harry J. Gwinnell

Attorney, Agent, or Firm—Lerner, David, Littenberg & Samuel

[57] **ABSTRACT**

A color decalcomania and method of forming the same are provided wherein the design layer is formed by separately depositing on a substrate at least three colors, namely, blue, red and yellow, and preferably a fourth color, namely black, each color comprising a mixture of pigment and glass frit. The frit will include at least 5 percent and preferably at least 10 percent of a cadmium substituent. The presence of the cadmium, usually in the form of CdO, in the frit mixed with each color makes all colors compatible with each other and prevents the formation of PbS during firing and protects the yellow color and red color. Furthermore, the frit, which preferably is stable and viscous allows the colors to fuse at approximately the same firing temperature allows colors to maintain their integrity, gives good color balance and provides compatibility in all color systems. The method for forming such color decalcomanias comprises forming the design layer of the decalcomania by separately mixing each color with a suitable frit, separately applying each color-frit mixture to a substrate, and drying before the next application of frit-color mix, and firing all colors at the same temperature.

25 Claims, No Drawings

COLOR DECALCOMANIA AND METHOD

FIELD OF THE INVENTION

The present invention relates to a color decalcomania having a design layer initially formed by employing at least three ceramic colors, namely, blue, red and yellow, and preferably a fourth color, namely black, and to a method for preparing such a color decalcomania.

BACKGROUND OF THE INVENTION

A decalcomania (decal) usually is comprised of a multi-layer structure including a backing, a design or pigment layer, and a protective layer applied over the design layer. The colors in the design layer are formed from inorganic pigments or oxides. A layer facilitating release of the backing from the design may be interposed between the backing layer and the design layer. The protective layer applied over the design layer can comprise a low melting point glass which acts as a protective barrier over the surface of the design layer, which protective barrier, being glass is resistant to both alkalis and acids, as well as to mechanical abrasion. Moreover, since this layer is transparent, the design and colors of the finished decal will appear as clearly as if no glass barrier were present.

A number of different types of decals are used at present in the pottery industry to apply patterns to ceramic ware. One of these is the so-called "underglaze" decal. This type of decal is applied to the ware after the ware has been formed but before it is glazed. Thereafter, a glaze is applied over the ware and decal. This glaze consists of a vitreous coating. The coating is formed directly from raw materials so that a very high temperature must be used in firing the ware to form the glass. The result of this process is a protective coating over the pigment such that the pigment will not be subject to chemical and mechanical attack such as produced by modern chemical detergents and mechanical washing devices. However, the use of such a high temperature as is necessary to form the glaze destroys the color value of many of the pigments that would be preferred to produce the desired colors. It will be appreciated from the foregoing that this underglaze ceramic decal is limited in application and color.

As a result of these limitations, the so-called "overglaze" decals were developed. That is, decals which are applied to the ware after the high temperature glaze has been put on. These overglaze decals can generally be divided into two classes — silk screen decals and lithographic decals.

In the silk screen process, a silk screen template or stencil is placed over the surface on which pigment is to be deposited and the pigment is applied through the screen. If the decal were of the "water mount" or "slide off" type, the surface on which the pigment is applied would be the layer of water soluble gum which has been placed over a paper backing. In this process, a relatively thick layer of pigment is deposited over the entire surface covered by the stencil. In order to increase the permanence of the design in the silk screen decal, a quantity of powdered low melting point glass may be mixed with the pigment so that, when the pattern is set by the application of heat, this powdered glass will fuse and become a part of the pattern itself. The silk screen decals, however, like the underglaze decals, are subject to a number of limitations. For example, the fine and clear cut designs and tonal variations available in the lithographic process cannot be obtained by the silk screen process. Also, the thicker pattern which results from this process is not always desirable. Because of these limitations lithographic decals are widely used in the industry.

Lithographic decals are formed by printing the desired pattern on a substrate by a lithographic process. In the case of the water-mount decals, the pattern is printed on the top of the water soluble gum layer. As is the case with other types of decals it is essential that the pigment of lithographic decals be protected from the chemical and mechanical attack previously referred to. If it is not, the design will lose its lustre and brightness and the pigment may even rub off entirely with handling.

The design layer of the decalcomania which may include many different colors, is formed very much like a painting. A separate plate, stencil or printing is used for each color in the original to be reproduced. Thus if the design contains 10 colors, each of the 10 colors would be printed separately. This is an expensive and painstakingly slow technique.

Today, practically all color reproduction such as in the printing of magazines, posters, pictures and printed pages, but not in color decalcomanias for ceramic wares, is done by the method known as four-color process printing. In this method, the color original is separated into four different images, each of which is printed from a separate printing plate, member or image carrier, with a different ink to recreate a visual impression of the color original. The four colors used are yellow, magenta (blue-red or red), cyan (blue-green or blue) and black. The different colors in the reproduction are produced by combination of the yellow, red, blue and black inks. If the color inks are properly transparent, combinations of them will produce almost every color in the spectrum.

Much time and effort have been spent in the decalcomania industry toward developing a technique similar to four-color printing for producing color decalcomanias. These efforts have proven to be virtually fruitless, until now, and thus color decalcomanias are still being prepared by the relatively archaic, slow and costly "painting" procedure described above.

Perhaps the most salient reason why the conventional four color printing technique has not been adaptable to the decalcomania art is attributed to the lack of success in obtaining good and acceptable yellows and colors derived from yellows. It has been found that when conventional yellow pigments, such as cadmium yellows or lead-antimony yellows, are fired in the presence of pigments forming the blue, red and black colors, with or without a frit or flux, the yellows and reds tend to be burned out with concomitant formation of lead sulfide (black) and other undesirable reaction products. The lead sulfide ruins the resulting design layer by dirtying the colors thereof, especially the yellows and those colors derived from yellows. Furthermore, it has not been possible to develop the full pallet of intermediate shades using previous methods.

DESCRIPTION OF PRIOR ART

Prior art relating to decoration of wares, such as ceramic or enameled wares, with color decorations, is discussed in U.S. Pat. No. 2,216,017 to Matthes and assigned to Bomat, Inc. This patent discloses techniques for the manufacture of multi-colored vitreous enameled articles. In prior art processes, wherein color applied to the ware or employed in forming a design overlap or are superimposed upon each other, a separate firing is necessary for each color. If separate firings are not accomplished, then the finished article will be full of blisters and enamel defects; even if separate firings are accomplished, the finish will not be uniform, but will be stepped up, each subsequent color coating higher than the last. Also every time a color coat is fired, the color fades out so that the first color applied has changed to an undesirable shade after repeated firings and the colors lose the desired brilliance. Furthermore, there is a limit to the number of firings of which the first coat applied can be subjected.

The invention concept disclosed in the Matthes patent is directed to an improvement over such prior art techniques and specifically to a wet enameling process which consists of fusing a vitreous enamel coating to a metal base, applying one or two cover coats of enamel over the initial coating, applying a fine wash coating of frit over the surface to which colors are to be applied, applying a design-forming coating to the enameled base by thinly brushing thereon a mixture of enamel frit and coloring oxide, drying the coating, and thereafter applying another design forming coating having different coloring characteristics, the colors overlapping each other, drying the second coating and then firing the article to vitrify the enamel to the metal base. This patent does not relate to the formation of colored decalcomanias. Furthermore, it completely ignores the problem of burning yellows on firing with the resultant formation of lead sulfite or other reaction products which dirty or contaminate the colors laid down.

U.S. Pat. No. 2,324,433 to Scheetz relates to the multi-color decoration of vitreous objects. A decalcomania can be employed for the decoration and is formed by applying to the surface of a transfer sheet a ceramic color bond or adhesive, separately applying to such bond different ceramic colors each of which may be in admixture with a flux, the colors being applied in the form of a multiplicity of spaced colored lines or dots, so that interstices form between color deposits. When the decalcomania is applied to the ceramic object and the combination fired to fuse the colors with the object, the bonding material in the form of a gas is passed off through the interstices between the color deposits.

U.S. Pat. No. 3,089,782 to Bush et al. and assigned to Ferro Corp. relates to the color decoration of ceramic surfaces. Colors in admixture with a flux are separately applied to the ceramic surface. The inventive feature in this patent is the use of a hot thermo-vehicle, which is a wax in admixture with a thermoplastic resin, with each color-flux mixture. As the color-flux-hot thermo fluid vehicle mix is applied to the relatively cool ceramic surface, the thermo-filled vehicle solidifies and fixes the color to the surface. In this way, a drying operation between each color application is avoided.

Bush et al. indicates that use of the thermoplastic vehicle permits up to eight color applications, requiring only one firing operation.

It is apparent that Bush, et al.. as well as the other above-mentioned patents do not disclose or relate to a four-color process for preparing decalcomanias.

DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has been found that a three- or four-color printing process similar to that employed in the printing industry can be employed in the manufacture of ceramic color decalcomanias. In such process, three colors, namely blue, red and yellow and optionally black, can be fired together without adversely affecting each other. That this has been accomplished is indeed surprising in view of the history of failures where three- or four-color techniques have been attempted in the manufacture of color decalcomanias.

Applicants, surprisingly, have overcome the problems which led to previous failures in attempting to apply the four-color technique in the manufacture of color decalcomanias and have been able to obtain good, clean, clear yellows and colors derived from yellows. This success is believed to due to applicants' discovery that where the four colors are each separately deposited in admixture with a suitable frit as defined hereinafter and the frit includes at least 5 percent by weight of a cadmium substituent, upon firing of all the colors at the same time and temperature, formation of lead sulfide and/or other reaction products which dirty the yellow and/or other colors, is inhibited. The presence of the suitable frit which includes the cadmium substituent mixed with each of the colors makes all colors compatible with each other and inhibits the formation of undesirable reaction products. Accordingly, applicants are able to reproduce substantially any color design as part of a decalcomania employing only three or four colors and not the 10 or 11 or more colors previously required in the realistic reproduction of such color design.

In accordance with the present invention, there is provided a method for forming a color decalcomania employing only three or four colors in producing the design layer thereof, which comprises the steps of forming a colored design layer on a substrate by separately mixing ceramic pigments with a suitable frit to form three or four separate ceramic color compositions comprising blue color and frit, red color and frit and yellow color and frit and optionally black color and frit. The frit includes a cadmium substituent which can be in the form of an oxide or salt, which is preferably also present in the pigments forming the yellow color. Each ceramic color-frit composition is deposited on the substrate and dried before the next ceramic color-frit composition is deposited. After each of the color-frit compositions are deposited and dried, the design layer is formed. A protective covering or coating may, if desired, be applied over the design layer to complete the decalcomania, as will be described hereinafter.

In addition, in accordance with the present invention, there is provided a method of decorating an article employing the color decalcomania described herein, which comprises applying the color decalcomania to the ware and firing the ware to cause the frit and colors to become miscible and flow together, and fuse and to bond the decalcomania to the ware. As overlapping or superimposed colors fuse all colors of the final design are formed having the desired hue, shade and tonal balance.

There is also provided in accordance with the present invention a color decalcomania, the design layer of which is formed from at least three basic colors and preferably four colors, namely blue, red and yellow, and black, each color being employed in admixture with a suitable frit and the frit including a cadmium substituent preferably also present in the yellow color. As described, the frit will act as a source of cadmium for all of the colors thereby making the colors compatible with each other.

The design layer of the color decalcomania produced in accordance with the present invention has excellent color and will substantially duplicate the different hues, shades and color tones present in the original design, painting and the like from which the design layer is reproduced. As will be apparent, the various colors, hues, shades and tonal balance of the original design to be coupled are reproduced in the design layer by depositing various combinations of the blue, red and yellow colors and preferably including black color, each in admixture with frit, such that the various colors touch each other, overlap or are superimposed one on the other depending upon the precise color required. The blue, and yellow colors become transparent when fired so that combinations of these colors will produce almost every color in the spectrum.

The color decalcomanias produced in accordance with the invention will preferably be of the overglaze type. It will be understood that underglaze decalcomania can be produced as well, however in such case, the pigments available for the three or four colors which can withstand the high firing temperatures required, are somewhat limited.

The nature of the frit employed in admixture with the basic three or four colors or pigments will be determined primarily by the type of decalcomania to be manufactured, that is overglaze or underglaze, and the type of pigments employed in the yellow. However, all cases, in order for the frit to be suitable for use herein, it must include a cadmium substituent. Further, the frit should be one hwich prevents undue mixing of each of the applied colors permitting the integrity of the individual applied colors to be maintained during firing and thereafter. The frit will allow the colors to fuse without chemically reacting with each other. Preferably, the frit is of a highly viscous nature and has a low solubility for the particular pigment system employed.

For example, where the decalcomania is of the overglaze type, the frit can basically be a lead silicate type glass composition which, however, will include a cadmium substituent, in the form of a salt or oxide. Thus, where the yellow color is cadmium sulfide, then in such case, the frit will include cadmium metal in the form of, for example, cadmium oxide. Where the yellow color is formed by oxides of lead and antimony, then in such case, the frit will include cadmium, usually in the form of cadmium oxide. Where the yellow is formed of oxides of nickel and titanium, the frit will include cadmium oxide.

The frit containing the cadmium substituent when mixed with each color allows the colors to be fused at the same firing temperature, allows colors to maintain their integrity, gives good color balance and provides compatibility in all color systems. In essence, the frit which includes the cadmium substituent will provide that common metal to each of the other colors, namely the black, blue and red colors, and yellow colors, where such yellow is not cadmium-based. In this manner, the frit imparts color compatibility to all of the colors.

Depending on the properties desired, where the decalcomania to be formed is of the overglaze type, the frit to be mixed with each color will include from 0 to about 60 percent and preferably from about 40 to about 60 percent oxide and from 0 to about 50 percent and preferably from about 10 to about **50** percent silicon dioxide (SiO_2) as the major substituents.

The frit will also include from about 5 to about 50 percent and preferably from about 10 to about 20 percent by weight cadmium oxide (CdO) to impart the desired color stability to the design layer of the decalcomania and inhibit the reds and yellows in the design layer from forming lead sulfide and/or other reaction products and thereby turning black.

The frit may also include from 0 to about 30 percent and preferably from about 10 to about 20 percent by weight boric oxide (B_2O_3) as a so-called "coordination source of oxygen."

The frit employed herein may also include a wide variety of alkali oxides to impart design properties thereto as will be seen hereinafter. For example, the frit may contain from 0 to about 25 percent and preferably from 1 to about 7 percent by weight sodium oxide and/or potassium oxide and from 0 to about 3 percent and preferably from about 0.5 to about 1.5 percent by weight lithium oxide to impart increased solubility to the frit and make it lower melting.

Furthermore, the frit may include alkaline earth metal oxides such as oxides of calcium, magnesium and/or strontium in lieu of a portion of the alkali metal oxides mentioned above to vary the expansion characteristics of the frit as desired. The alkaline earth metal oxides may be employed in amounts of up to about 20 percent and preferably from about 3 to about 5 percent by weight of the frit.

In addition, the frit may include from 0 to about 6 percent by weight alumina (Al_2O_3) to impart the desired viscosity characteristics to the frit.

As indicated, it is possible that the frit comprise only cadmium oxide. However, for all practical purposes, the frit will also include the lead oxide, silica, and boric acid.

A frit which does not include lead oxide can comprise a sodium oxide-cadmium oxide-boric oxide-silica glass containing from about 15 to about 40 percent CdO and preferably from about 18 to about 30 percent CdO, from about 10 to about 50 percent SiO_2, from about 10 to about 25 percent Na_2O and from about 10 to about 20 percent B_2O_3. However, alumina, other alkali and the like may be included in proportions as set out herebefore with respect to the lead containing frit.

The frit mixed with each of the color pigments may also contain tin oxide and optionally titanium dioxide in addition to lead oxide, silicon dioxide and cadmium oxide. Such a frit is disclosed in copending application Ser. No. 303,620, filed Nov. 3, 1972. Such a frit may contain 2 to 15 percent and preferably 6 to 8 percent SnO, 0 to 10 percent and preferably 1 to 3 percent TiO_2, 15 to 65 percent and preferably 30 to 40 percent SiO_2 and 10 to 60 percent and preferably 25 to 35 percent PbO. In addition, such frit may include boric oxide, alkali oxides, alumina and the like as set out herein.

The pigments employed in forming the four colors will be of the conventional type ceramic colors, namely oxides, sulfides and/or other salts of metals such as Pb, Cd, Sn, Ti, Ni, Cr, Co, Fe, Se, Al and the like, as will be apparent to one skilled in the art.

One of the preferred four color formulations of the invention comprises a cadmium sulfide-zinc sulfide yellow, comprising from about 80 to about 100 percent CdS and from about 0 to about 20 percent ZnS, a cadmium sulfoselenide (CdS.Se) red containing from 70 to 100 percent CdS, and 0 to 30 percent Se, a blue comprising a mixture of cobalt oxides (Co_3O_4), chromium oxide (Cr_2O_3) and alumina (Al_2O_3) in a proportion of Co_3O_4 ranging from 5 to 100 percent and Cr_2O_3 ranging from 0 to 60 percent, and Al_2O_3 ranging from 0 to 80 percent, and a black comprising a mixture of cobalt oxide (Co_3O_4), chromium oxide (Cr_2O_3) and iron oxide (Fe_3O_4) in a proportion of Co_3O_4 ranging from 0 to 60 percent, Cr_2O_3 ranging from 5 to 70 percent, and Fe_3O_4 ranging from 5 to 50 percent.

Another preferred four-color formulation comprises commercially available mixtures of lead oxide and antimony oxide yelow, ferrous oxide (FeO) red, and a black and a blue as described above in connection with the CdS yellow-CdS.Se red formulation.

Another preferred four-color formulation comprises a nickel-titanium yellow (commercially available) in admixture with any of the aforementioned colors.

Preferred four-color systems including frit compositions to be mixed with each other, in accordance with the invention are summarized below.

In a preferred embodiment of the invention, a low melting point glass or frit is applied over the three- or four-color design layer as a protective coating therefor. The protective frit coating will generally protect the design layer from chemical attack and mechanical abrasion, and inhibit fade-out and wash-out of color from the design. In addition, the protective frit coating will prevent direct contact of the design layer, displayed on household wares, with food and drink, will seal the design to the ware, inhibit lead and/or cadmium release from the design layer, inhibit sublimation, that is, prevent vaporization of cadmium and selenium from the design layer, where present, and facilitate blending of colors during firing.

The protective frit coating employed to cover the design layer will preferably, but not necessarily, be of the same formulation as the frit mixed with each of the four colors. Thus, for example, if the yellow color is a cadmium sulfide yellow, the protective frit and the frit mixed with the colors will include cadmium oxide.

The protective frit formulation may be of any desired viscosity to fulfill any particular need. As will be apparent to one skilled in the art, viscosity or fluidity of the frit and the melting point thereof, may be varied by varying the amounts of alumina, alkali oxides, and tin oxide and titanium oxide, if present.

FORMULATION	COLOR	PIGMENTS (% BY WEIGHT)	FRIT FORMULATION (% BY WEIGHT) 1	2
A	Yellow	CdS — ZnS (90:10)	PbD—45%	PbO—40%
	Red	CdS.Se (90:10)	SiO_2—20%	SiO_2—25%
	Blue	Co_3O_4—30%	B_2O_3—15%	B_2O_3—12%
		Cr_2O_3—40%		
		Al_2O_3—30%	CdO—15%	Cdo—14%
	Black	Co_3O_4)	Na_2O—2%	SnO_2—6%
	(optional)	Cr_2O_3)equal amounts		
		Fe_3O_4)	Al_2O_3—3%	Na_2O—3%
B	Yellow	PbO—70%	Pbo—45%	PbO—40%
		SbO—30%		
	Red	FeO	SiO_2—20%	SiO_2—25%
	Blue	Co_3O_4—30%	B_2O_3—15%	B_2O_3—12%
		Cr_2O_3—40%		
		Al_2O_3—30%	CdO—15%	Cdo—14%
	Black	Co_3O_4)	Na_2O—2%	SnO_2—6%
	(Optional)	Cr_2O_3) equal amounts		
		Fe_3O_4)	Al_2O_3—3%	Na_2O—3%

The coloring agents or pigments of the design layer will comprise ceramic pigments, having an average particle size within the range of from about 0.5 to about 2 microns which are mixed with the frit into the binder or vehicle. Preferably, the pigments will be of fine particle size, such as of an average particle size of less than about 1 micron. The pigments which may be used and the manner of their use are known to those skilled in the art.

The frit to be mixed with the pigment particles will have a particle size within the range from about 0.5 to about 2 microns and preferably from about 0.5 to about 1 micron.

In carrying out the method of the invention, the frit will be mixed with each of the three or four colors for example, by blending in an amount to provide a weight ratio of color: frit within the range of from about 1:4 to about 4:1 and preferably, from about 1:2 to about 2:1, and optimally about 1:1. The frit and color may also be sintered together for added stability. It will be apparent that by increasing the amount of frit in the frit-color mixture, the transparency of the particular color will be increased.

In addition to those frits set out hereinbefore, examples of other frits which may be employed as a protective coating are set out in U.S. Pat. No. 2,734,840 to Kane.

The low melting glass or frit is prefused prior to application as a protective coating over the design layer. Thus, the various oxide components mentioned hereinbefore may be fused to form a glass in accordance with conventional techniques. Thereafter, the prefused glass is powdered so that it will have an average particle size within the range of from about 4 to about 12 microns prior to use.

It is essential that the frit so formed be fully matured (fluid) at the firing temperature so that it will fuse to the design layer to form a protective layer thereon and bond the design layer to the ware.

The glass or frit protective layer or frit to be mixed with the pigments is colorless so that it does not interfere with or mask the colors of the design layer. However, the frit protective layer may include a metallic oxide in an amount within the range of from about 1 to about 8 percent by weight.

An amount of the low melting glass or frit should be deposited on the design layer so that the protective glass coating thereafter formed will have a thickness within the range of from about 6 to about 28 microns and preferably from about 9 to about 20 microns. Thus, the ratio of thickness of the glass protective coating to the design layer may be within the range of from about 1:1 to about 3.5:1 and preferably from about 2:1 to 2.5:1.

The decal of the present invention may be provided with any suitable backing, such as a dry strippable backing or a solvent mount, or the decal may be a water mount slide-off decal. The backing may be of paper or other suitable material such as, for example, plastic or fabric.

The three or four colors forming the design layer are each applied to a substrate such as a backing sheet, in the form of a mixture of color or pigment and frit. However, a printing medium or vehicle may also be included where the design is formed by screening, in an amount within the range of from about 20 to about 35 percent by weight vehicle of the frit-pigment and vehicle composition. Where such a vehicle is employed, the amount of frit present in proportion to the amount of pigment may be increased so that the ratio of frit:pigment will be within the range of from about 10:1 to about 2:1.

The printing medium or vehicle may be formed, for example, from one or more of such materials as drying oils, varnishes, or resins. Some examples of suitable resins are alkyds, phenolics, urea-formaldehydes, melamine-formaldehydes, polyesters, melamine-alkyds, vinyls, and acrylics. Various additives may be incorporated into the vehicles, for example, dryers, promoters, and/or accelerators.

The compositions of the printing medium or vehicle for the color-frit mixture will vary depending upon the pigments used as coloring agent and the amount of frit present in the color-frit mixture. While the ink formulation must be varied depending upon the pigment employed, as is known to those skilled in the art, some typical ink formulations wherein the parts are expressed as parts by weight are as follows:

INGREDIENT	1	2	3
Gel No. 100 (linseed-alkyd resin varnish gelled by aluminum octoate, supplied by Zobel Co.)	10	12	15
Linseed No. 4 (linseed oil of 62.1 stokes viscosity)	10	—	—
Linseed No. 1 (linseed oil of 14.4 stokes viscosity)	15	—	—
Lead Drier	2	4	4
Manganese Drier	2	4	4
Aroplaz 2506 (alkyd resin supplied by Archer-Daniels)	—	30	25
Aroplaz 1274 (alkyd resin supplied by Archer-Daniels)	—	30	25
Puffo No. 2 (thixotropic control agent supplied by Mooney)	—	3	3
Petroleum Jelly	—	—	5
Pigment	60	120	120
Frit	30	20	15

The design layer of the color decalcomania of the invention may be formed by conventional dry or wet printing techniques employing lithographic or screening techniques. Regardless of the method employed, the basic technique for forming the design layer comprises forming three or four separate ceramic color compositions comprised of a mixture of frit, pigment and optionally a printing medium, laying down a layer of one of the ceramic color compositions of frit-pigment mixture with or without printing medium, or a varnish (such as linseed oil) coated substrate, drying the deposited layer, employing conventional drying techniques, and repeating the separate laydown and drying procedure for each of the additional two or three ceramic color compositions, to form the design layer. After the last deposit is dried, a protective coating in the form of a prefused glass frit or flux is separately deposited on the design layer. If desired, the prefused glass or flux layer may be initially deposited on the substrate or backing sheet and the design formed on the glass layer. When the backing sheet containing the design layer and protective coating is positioned on a glazed piece of ware and fired the frit mixed with the pigments causes the colors to mix, flow together and fuse and the protective coating of prefused glass flux fuses and tightly binds the design layer to the ware.

The protective frit may be applied over the design by various methods, such as, silk screening, offset printing, or by printing a clear film over the design and then dusting a prefused frit over the film. If desired, the dusting operation may be eliminated by incorporating the frit into a film such as a printing varnish, oil or resin.

The design layer may be formed by the wet printing technique set out in U.S. application Ser. No. 193,153, filed Oct. 27, 1971 by Blanco.

It will be apparent that the original color design is separated or broken down into three or four different images, one for each of the colors and printing plates or stencils made for each image depending upon whether a lithographic or screening technique is employed.

Varnish will be deposited by offset printing, screening or the like on the printing plates or stencil, and then will be transferred to a blanket and subsequently to a backing sheet or substrate such as a paper backing. After laydown or powdering of the first ceramic color composition, and drying, a varnishing, laydown and drying steps will be repeated for each of the remaining three ceramic color compositions to form the design layer.

The order of laydown of the four colors is preferably dark to light, that is, blue, yellow and red, unlike conventional color printing where the reverse is true. Where a fourth color is employed, namely, black, the black will be laid down before the blue. However, the order of laydown may be reversed from light to dark in the present method with no substantial deleterious effects observed.

Once the decal is complete, it is transferred to the article of pottery or ware in the usual manner. That is, the decal is placed on the ware in the wet condition and the paper removed by sliding it from under the decal. The article is then fired at a relatively low temperature and the frit in admixture with pigment and the powdered glass protective coating fuse so as to form an integral part of the ware and provide a glass layer which protects the pigment from chemical or mechanical action. In the case of overglaze decalcomanias, a relatively low temperature can be used where frit mixed with the colors and the layer of protective frit is made up of prefused glass which will melt at much lower temperature than is required to fuse the raw materials from which the glaze on the ceramic ware itself is formed. The usual firing temperature required for this operation is between 1,000° F. and 1,500° F. It should be particularly noted at this point that this low temperature unlike the high temperatures used in applying the glaze to the entire plate, does not operate to destroy or impair the color values of the pigments used. In this decal as in all overglaze decals the glaze is applied before the decal is transferred to the plate, and thus the decal is not subject to high temperatures. But in this case to protect the decal and provide a permanent design a low melting point glass may be used over the pigments. The pigment is protected in much the same manner as the underglazed decals and yet the color values are not impaired by the application of very high temperatures such as are required in applying glaze. Pigments of the type which are affected by contact with molten glass are affected in this case at the surface only and not sufficiently to impair color value of decal.

A final supporting and protecting layer may be disposed over the entire decal. This layer may be varnish, lacquer, or some similar substance. This layer serves to protect the decal sheet during storage and shipment and is volatized when heat is applied to the decal. It also aids during transfer of water mount decals in that it protects the powdered glass layer from water.

The decalcomanias of the invention may be employed as decorations for ceramic ware, glassware, pottery, aluminum enamel, or any other ware which melts at 1,500° F. or below.

It will be appreciated that the present description has been by way of example only and is not intended as a limitation to the scope of the invention.

What is claimed is:

1. A method of forming a color decalcomania including a backing or substrate layer and a color design layer deposited thereon, wherein the steps of forming the design layer comprise separately depositing on a substrate at least three ceramic color compositions in patterns which overlap to a desired extent to produce upon firing at least such three colors and additional colors where such overlap occurs, each color composition deposited as a separate layer, each color composition comprising a ceramic pigment in admixture with a frit, the frit of each color composition containing at least about 5% by weight of a cadmium substituent, such colors including at least blue color, red color and yellow color, and drying each deposition of ceramic color composition before depositing the next ceramic color composition to form the design layer.

2. The method in accordance with claim **1,** wherein four color compositions are deposited on the substrate and the fourth color is black.

3. The method in accordance with claim **1** wherein the yellow color comprises cadmium sulfide and zinc sulfide and the cadmium substituent in the frit is in the form of an oxide or salt thereof.

4. The method in accordance with claim **1** wherein the yellow color comprises a mixture of lead oxide and antimony oxide.

5. The method in accordance with claim **1** wherein said frit contains from about 5 to about 50 percent by weight of the cadmium substituent.

6. The method in accordance with claim **3** wherein the red color comprises a mix of cadmium sulfide and selenium, the blue color comprises a mixture of oxides of cobalt, chromium and aluminum, and the black color comprises a mixture of oxides of cobalt, chromium and iron.

7. The method in accordance with claim **4** wherein the red color comprises ferrous oxide, the blue color comprises a mixture of oxides of cobalt, chromium and aluminum and the black color comprises a mixture of oxides of chromium and iron.

8. The method in accordance with claim **3** wherein the frit comprises from 0 to about 40 percent by weight silica, from 0 to aabout 60 percent by weight lead oxide, from 0 to about 15 percent by weight boric oxide, from about 5 to about 50 percent by weight cadmium oxide and from 0 to about 10 percent by weight alkali oxides.

9. The method in accordance with claim **3** wherein the frit comprises from about 10 to about 60 percent by weight lead oxide, from about 15 to about 65 percent by weight silica, from about 0 to about 10 percent by weight titanium dioxide and from about 2 to about 15 percent by weight tin oxide.

10. The method in accordance with claim **1** for forming an overglaze decalcomania comprising a backing or substrate layer, a design layer disposed on the backing or substrate layer, including the step of applying a low-melting point glass frit over the design layer to form a protective layer thereon.

11. The method in accordance with claim **1** wherein the design layer is formed by lithography.

12. The method in accordance with claim **1** wherein the design layer is formed by silk screening.

13. The method in accordance with claim **1** wherein the design layer is laid down by wet printing techniques.

14. The method in accordance with claim **1** wherein the design layer is laid down by dry printing techniques.

15. The method in accordance with claim **1** wherein the ceramic color compositions include a printing medium or vehicle in addition to frit and pigment.

16. The method in accordance with claim **1** wherein each of the ceramic color compositions comprises a mixture of firt and pigment in a weight ratio of frit:pigment within the range of from about 4:1 to about 1:4.

17. A method for forming a color decalcomania including a colored design layer deposited on a backing or substrate layer, which comprises separately mixing ceramic pigments with a frit to form at least three separate color compositions comprising blue color and frit, red color and frit, and yellow color and frit, the frit with each of said colors containing a cadmium substituent in an amount of at least about 5 percent by weight coating a backing or substrate layer with a varnish, depositing a first of said color-frit compositions on said varnish coating, drying said deposition of color-frit composition, repeating said varnish coating, color-frit depositing and drying steps for each of the reamining color-frit compositions to form the design layer wherein a varnish layer separates each layer of color-frit composition, the color-frit compositions being deposited in patterns which overlap to a desired extent to produce upon firing at least such three colors and additional colors where such overlap occurs, so that upon application to a ware and firing all color-frit compositions at the same temperature, a design layer is formed having the desired colors, shades, hues and tonal balance.

18. The method in accordance with claim 17, wherein four separate color compositons are deposited on the varnish coated substrate and the fourth color composition is black color and frit.

19. A ceramic color decalcomania comprising a backing or substrate layer and a design layer disposed on said backing or substrate layer, said design layer formed from separate layers of at least three basic colors, blue, red and yellow, each layer containing only one of said colors, each color being employed in admixture with a frit, and the frit admixed with each color containing at least about 5% by weight of a cadmium substituent, and the design layer including patterns of such colors which overlap to a desired extent, such that upon firing at least such three colors and additional colors are produced where such overlap occurs.

20. The color decalcomania as defined in claim 19 wherein said frit is of relatively high viscosity and prevents undue mixing of each of the colors permitting the integrity of the individual applied colors to be maintained.

21. The color decalcomania as defined in claim 19, wherein the frit contains from about 5 to about 50 percent cadmium substituent.

22. The color decalcomania in accordance with claim 19 including a protective coating of prefused low melting point glass over the design layer.

23. The color decalcomania in accordance with claim 22, wherein said glass includes increments of lead oxide, silicon dioxide, cadmium oxide and tin oxide and optionally titanium oxide.

24. The color decalcomania as defined in claim 19 wherein said design layer is formed from separate layers of four colors and the fourth color is black and is in admixture with said frit containing at least about 5% by weight cadmium substituent.

25. A method of decorating an article or ware, which comprises forming a color decalcomania including a backing or substrate layer and a color design layer deposited thereon, wherein the steps of forming the design layer comprise separately depositing on a substrate at least three ceramic color compositions in patterns which overlap to a desired extent to produce upon firing at least such three colors and additional colors where such overlap occurs, each color composition deposited as a separate layer, each color composition comprising a ceramic pigment in admixture with a frit, the frit of each color composition containing from about 5 to about 50% by weight of a cadmium substituent, such colors including at least blue color, red color, and yellow color, and drying each deposition of ceramic color composition before depositing the next ceramic color composition to form the design layer; applying the color decalcomania to the ware; and firing the ware and decalcomania to cause the frit and colors of the decalcomania to fuse and to bond the decalcomania to the ware.

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